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Review

Plant Secondary Compounds in Soil and Their Role in Belowground Species Interactions

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Knowledge of the effect of plant secondary compounds (PSCs) on belowground interactions in the more diffuse community of species living outside the rhizosphere is sparse compared with what we know about how PSCs affect aboveground interactions. We illustrate here that PSCs from foliar tissue, root exudates, and leaf litter effectively influence such belowground plant–plant, plant–microorganism, and plant–soil invertebrate interactions. Climatic factors can induce PSC production and select for different plant chemical types. Therefore, climate change can alter both quantitative and qualitative PSC production, and how these compounds move in the soil. This can change the soil chemical environment, with cascading effects on both the ecology and evolution of belowground species interactions and, ultimately, soil functioning.

Highlights

Plants produce a high diversity of secondary compounds that are released to their surroundings.

The role of PSCs on aboveground interactions has been well studied, but less is known about the role of PSCs in mediating and determining the outcome of belowground interactions, especially interactions beyond the rhizosphere.

PSCs enter the soil directly by excretion from belowground plant organs or indirectly by washing from the canopy and leaching from litter.

Leaching of PSCs creates a heterogeneous soil chemical environment and mediates plant–plant interactions, plant–microbiome associations, and plant–soil invertebrate relationships. This also affects and shapes the diffuse community of species living in soil further away from the rhizosphere.

Climate change can substantially alter the quantitative and qualitative production of PSCs released to the soil, which may change belowground species interactions and affect species composition, richness, and, ultimately, soil functioning.

Plant Chemicals Mediate Species Interactions

Secondary compounds in plants are major contributors to the chemical diversity of nature. They are formed from **primary metabolites** (see Glossary) in specific pathways and are omnipresent in plants. The distribution of **PSCs** is heterogeneous across the plant kingdom, and these compounds exhibit extensive variation both among and within species [1]. Although many PSCs also have pivotal roles in the primary metabolic processes of the plant (such as growth or development), most are known to serve as infochemicals mediating interactions between plants and their biotic and abiotic environments. PSCs can profoundly modify the abiotic environment as they are released into the atmosphere, soil, and water of an ecosystem, which in turn determines the community structure of the biotic constituents. For example, PSCs that accumulate in stems and foliage of the vegetation can promote bushfires, which profoundly alter the physicochemical properties of soil and groundwater [2]. Many PSCs are also involved in ecologically crucial interactions for plants, because they can form chemical barriers against pathogens and herbivores, attract pollinators and predators of herbivores, and help disperse fruit and seeds [3]. To fine-tune the release of PSCs, plants 'eavesdrop' on their neighbors and increase their own defenses when they sense volatiles released from neighboring plants damaged by leaf herbivores [4].

PSC-mediated interactions between plants and their associated organisms are best documented for aboveground compounds associated with airborne transport and signaling [3,5,6]. However, PSCs are also omnipresent in the soil, where they mediate interactions with soil organisms and neighboring plants. Compared with aboveground interactions, these soil PSCs represent a 'hidden' link between organisms. Recent reviews of PSCs and belowground interactions [7–9] have focused on PSCs in root exudates and on species interactions, mainly in the **rhizosphere**. However, less attention has been given to the impact of PSCs on the broader and more diffuse community of associated species further away from roots, which also includes the effects of PSC from foliar tissue and litter decomposition. Climate change may alter both the quantitative and qualitative production of PSCs, which could cascade to affect belowground

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PSC-mediated community interactions. Given the vital role of PSCs aboveground, we expect them to be equally important to belowground plant–organism interactions.

Here, we focus on four major groups of PSCs [terpenes, flavonoids, glucosinolates, and alkaloids (Table 1)] that enter the soil matrix. We discuss their origin and fate in the soil and their ecological and evolutionary impacts on belowground interactions. Release of PSCs by plants alters soil chemistry, and neighboring species can either tolerate, adapt to, or escape the chemical environment this imposes on them. However, the production, release, and transport of PSCs by plants are affected by local conditions, such as microclimate, microbes, and herbivore and pathogen pressure. Therefore, changes in climate will affect the quantitative and qualitative production and release of PSCs not only directly through changes in temperature and humidity, but also indirectly through potential concomitant changes in herbivore and pathogen pressure. Given that the effects of PSCs on neighbor species are often both compound and dose specific, there is the potential for cascading effects of PSC-driven alteration of soil chemistry on belowground interactions. So far, however, little is known regarding such cascading effects in plant–soil community interactions. To encourage more studies on this topic, we outline knowledge gaps and describe best practices for sampling and detecting PSCs in soil, to designate directions for future studies advancing this field of research.

Origin of PSCs in Soils

How do PSCs enter the soil? Those formed in roots can be excreted directly into the soil from living and deteriorating tissues [10]. PSCs formed in aboveground organs are deposited into the soil from belowground organs following internal transport [11] or during wet and dry deposition from the atmosphere after volatilization and further chemical reactions [12–14]. PSCs can also be washed from vegetation surfaces with water intercepted during precipitation [15], or they may outgas and leach from fresh and decomposing litter on the soil surface and in the upper horizons [16,17]. Many plant species accumulate large quantities of PSCs in secretory organs that are either external, such as trichomes, or internal, such as oil blisters or resin ducts, and a strong discontinuous release is expected during the decline and decomposition of these organs.

Concentrations of PSCs can be high and persistent in the soil. For instance, mono- and sesquiterpenes released from pine needles, litter, and roots are detectable in forest soil throughout the year [18] and can reach high concentrations especially in topsoil but also lower mineral soil, being highest in late summer, and in the winter during snow cover [19]. Glucosinolates, produced by all cruciferous plants, are hydrolyzed in the soil to highly bioactive compounds, notably isothiocyanate, nitriles, and thiocyanate. The degradation and hydrolyzation of glucosinolates depend on the presence of the extracellular enzyme myrosinase [20]. Glucosinolates are water soluble and can be more easily washed out from soil, whereas isothiocyanates are hydrophobic and adsorb strongly to organic matter [20,21] and, thus, may persist in the soil for periods of time. For example, the isothiocyanate sinigrin is persistent in the soil of forests invaded by *Alliaria petiolata* (garlic mustard), where even low concentrations suppress the germination and growth of arbuscular mycorrhiza. This suppression disrupts the mycorrhizal association with native plants, negatively affecting the resource uptake by that plant [22]. The persistence and slow degradation of many PSCs in soil emphasize the ecological and evolutionary potential pressure PSCs can impose on belowground species.

PSC Production under Climate Change

The production of PSCs improves the ability of plants to cope with different abiotic [23] and biotic stressors [5,6]. Various abiotic factors, such as CO_2 and temperature, affect PSC release

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by up- or down-regulating their production, although the specific PSC compounds that are affected may differ among factors. For example, in Northern Hemisphere trees, high CO_2 levels generally increase the foliar concentration of phenolic compounds, such as flavonoids and tannins, and decrease the production of terpenoid compounds, whereas elevated temperatures lead to the opposite trend [24–26]. Drought can both increase and decrease PSC production dependent on the severity of drought and on the compound. Terpenoids and phenolics in temperate and Mediterranean trees and herbs increased under moderate drought stress but decreased under severe drought [25,27,28]. Although severe drought overall decreased the total terpenoid emission, some specific mono- and sesqui-terpenes either increased or remained unaffected, suggesting an adaptive role of specific compounds in mitigating abiotic stress [27,28].

In addition to environmental effects on the production of specific compounds or compound classes, genetically determined variation in the PSC chemical phenotype (hereafter referred to as chemotype) is present in many species. For example, a strong genetic basis for variation in the identity of leaf chemical compounds has been demonstrated for terpenes produced in oak and pine trees [29–31], aromatic Lamiaceae [32], Asteraceae [33], for glucosinolates produced in the Brassicaceae [34], and for flavonoids in Berberidaceae [35], illustrating that genetic variation for these compounds is present in a range of plant families. Thus, the (a)biotic environment can shape which compounds are released to the environment not only through differential induction of PSCs, but also by natural selection, favoring genotypes producing specific chemotypes (Figure 1) [36]. Differences in climatic conditions and herbivore pressure favor specific chemotypes both within and among species [29,37,38]. A recent example of evolutionary changes in PSC production in response to climate change is that of wild thyme (*Thymus vulgaris*), a small shrub widespread in the Mediterranean Basin. The dominant monoterpene in thyme is genetically determined to be a either phenolic or a nonphenolic type. These two chemotypes are ecotypes with adaptation to warm dry summers and early winter frost, respectively [39]. The lack of very cold winters over the past 25 years has been associated with a significant increase in phenolic chemotypes in regions that were previously dominated by nonphenolic types [38]. In addition to differences in their ability to tolerate frost and drought, the toxicities of phenolic and nonphenolic chemotypes differ towards associated plants, microorganisms, and herbivores, suggesting that climate-driven changes in the genetic composition of this widespread species will have cascading effects on associated species interactions.

A correlation between variation in PSC production and environmental variation holds for many plant species, but we need more long-term experimental studies to understand whether current and future changes in climate and herbivore pressure will result in major induced or genetic changes in PSC production. If so, cascading effects of such changes are expected for below-ground species interactions, decomposition of organic matter, and, ultimately, nutrient cycling in soil [25,40]. Moreover, climate change may also affect the concentration of PSCs in soil by altering soil-water content, temperature, and pH. As a result, the levels and circulation of liquid and gas among soil pores (see later) will change and, hence, also the movement and diffusion of PSCs.

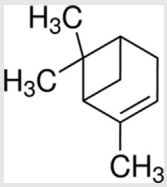
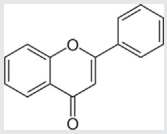
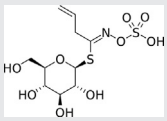
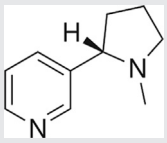
Diffusion of PSC in Soil

In contrast to atmospheric PSCs, volatile PSCs in the soil can form stable concentration gradients due to the lack of air turbulence. The diffusion of PSCs in soil depends on their physicochemical properties (Table 1) and the texture of the soil matrix. Fine-textured and clayey soils facilitate the flow of volatile PSCs that are diluted in smaller air volumes due to the smaller pores of these soil types. This generates gradients that are steeper and propagate faster than those in soils with

Glossary

Allelochemical: a compound produced by an organism that can have a detrimental physiological effect on individuals of another species when released into the environment.
Allelopathic effect: the interference effect of chemical compounds released by a plant on the growth and performance of other plants. An allelopathic effect usually implies a direct negative (harmful) effect, but some definitions also include positive effects.
Narcotic effect: unspecific effects of lipophilic organic chemicals on membrane fluidity. These chemicals tend to partition into the lipid compartments of the organism, causing (nonpolar) narcosis or baseline toxicity.
Phytotoxic: chemical compounds that are toxic to plants, including any adverse effect on plants, such as delayed seed germination, inhibition of growth, death, or destruction of plant tissue.
Plant secondary compounds (PSCs): organic compounds typically formed from primary metabolites in specific pathways. Some PSCs are involved in the primary metabolic processes of a plant, but most are known to serve as infochemicals mediating interactions and are important for plants to survive in the environment (e.g., by their repellent, attractant, or toxic effects on other organisms).
Primary metabolites: compounds from metabolic pathways present in all plants and essential for growth, development, and reproduction. These metabolites comprise amino acids, nucleic acids, peptides, various carbohydrates, and lipids.
Rhizosphere: the microecological zone of soil in direct proximity to plant roots; includes the organisms in that soil that are directly affected by root exudates.

Table 1. Overview of the Important Classes of PSC Involved in Mediating Belowground Interactions, and Best Practices for Sampling and Analyzing Them[a,b]

Compound class	Example of structure	Polarity	Water solubility	Volatility	Ecological interactions/ impacts and effects on associated soil organisms	The analytical instrument for detection in soil[c]
Terpenes: synthesized from isoprene units (C_5H_8); includes monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$)	 α-Pinene	Low	Low	High	Defensive and signaling compounds, many with a characteristic odor (e.g., α-pinene from pine, limonene from citrus); antioxidant, antimicrobial, and phytotoxic properties [3]; toxic to invertebrates due to baseline toxicity (**narcotic effect**) via interaction with cellular membranes [114]; involved in formation of aerosol particles, thus affecting climate [115]	Monoterpenes and highly volatile sesquiterpenes: SPME with PDMS adsorbent, purge-and-trap with Tenax TA adsorbent and subsequent GC-MS [19,116]; online measurement with PTR-MS [117]; nonpolar sesquiterpenes likely adsorbed to soil particles require extraction with organic solvents and subsequent evaporation followed by GC-MS [41]
Flavonoids: general structural C-15 skeleton comprising two phenyl rings and a heterocyclic ring (C6-C3-C6)	 Basic flavonoid structure	Low to intermediate	Low to intermediate; presence of sugar moieties increases solubility in water	Low	Both defensive and signaling; promote symbiosis (used by legumes to attract rhizobia), various antimicrobial activities [118,119]; can interact with Ca^{2+} channels in cell membranes causing cytotoxic influx of Ca^{2+} [120]	Most likely present belowground in water and adsorbed to soil particles; extraction using polar solvents (water or methanol) unless complexes with metals are formed [121]; extracts can be analyzed with reversed-phase LC-MS [122]; aglycones may be sampled using SPE [118] and are amenable to GC-MS after derivatization; greater sensitivity may be obtained with SBSE and subsequent GC-MS
Glucosinolates: derived from glucose and an amino acid; most are found in order Brassicales (30)	 Sinigrin	High	High	Low	Due to polarity and water solubility, are readily taken up by soil organisms, where they can be converted to highly reactive compounds, such as isothiocyanate and thiocyanates; toxicity pathways include inhibition of cytochrome P_{450} detoxification complex, induction of programmed cell death (apoptosis), and genotoxic effects [123]	Mostly present in water phase due to high polarity and low volatility; extraction using polar solvents (water or methanol), subsequently analyzed with LC-MS [17] or GC-MS after derivatization; SPE can increase concentration in the sample
Alkaloids: highly diverse, usually with basic nitrogen atom either in cyclic rings or open chains	 Nicotine	Low to intermediate	Low to intermediate	Low	Mostly defensive compounds; phytotoxic, toxic (e.g., strychnine), and narcotic effects (e.g., morphine and codeine); can interfere with gene transcription and protein synthesis [124]	Low concentration in soil, so clean-up and preconcentration may be necessary; polarity can be adjusted with pH changes and used in combination with liquid–liquid extraction, SPE, or SPME [125]; detection may require both LC-MS and GC-MS

[a]The chemical properties of PSCs affect their position and transport in the soil matrix, with polar PSCs dissolved in water, volatile PSCs diffusing through air spaces in the soil, and less polar nonvolatile PSCs adsorbed to the organic fraction of soil.
[b]Abbreviations: GC, gas chromatography; LC, liquid chromatography; MS, mass spectrometry; PDMS, polydimethylsiloxane; PTR, proton-transfer reaction; SBSE, stir-bar sorptive extraction; SPE, solid-phase extraction; SPME, solid-phase microextraction.
[c]See also Box 1 in the main text.

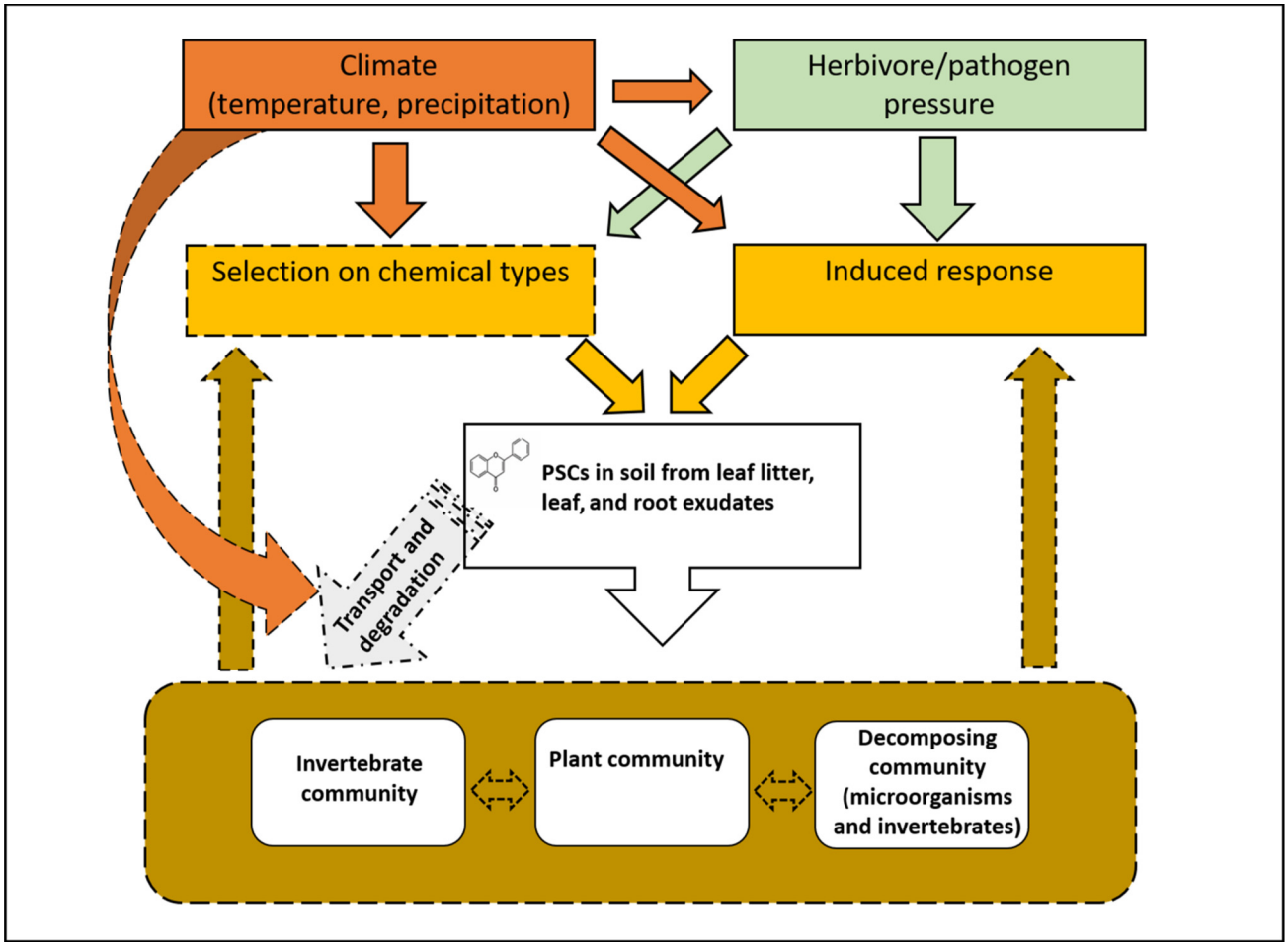


Figure 1. Climate Change Effects on Belowground Interactions Mediated by Plant Secondary Compounds (PSCs). Direct and indirect effects of climatic conditions (red box) and aboveground herbivore pressure (green box) on PSC production (yellow boxes) and input into the soil, and its belowground interactions (brown box). In addition, climate affects how PSCs are transported and degrade in soil. Dashed arrows and boxes indicate processes and effects that are less well understood and are elucidated in the main text.

large air spaces. However, in well-ventilated soils, PSCs will rapidly fill large air volumes, albeit at lower concentrations.

PSC transfer in soil is also affected by adsorption to the mineral and organic surfaces of soil particles, the fractions of which depend on soil type and layer, with A horizons (topsoil) generally containing more organic material than the underlying B horizons (subsoil) [41,42]. PSCs will adhere to and dissolve on lipophilic and hydrophilic surfaces during diffusion, thus forming intermediate pools in equilibrium with the gas-phase concentrations [43,44]. Therefore, soil organisms receive PSCs more slowly and with an attenuated amplitude compared with the actual variations in the emission strength of the PSC source.

Abiotic factors, such as temperature, soil moisture, and pH, interfere with the persistence and diffusion of PSCs in soil. The adsorption of volatile PSCs by the mineral and organic fractions of soil depends on pH, with higher adsorption in alkaline than acidic soils [45]. The acidity of

soil-pore water can affect the uptake of volatiles on aqueous surfaces, such as by protonating highly reactive sesquiterpenes that are otherwise poorly soluble in water [46]. Periods of rain and drought change the movement patterns of PSCs through soil, with opposite behaviors expected for volatile and nonvolatile water-soluble PSCs (Table 1). During rainy weather, volatile PSCs are first concentrated in the soil pores during water penetration and then move with air bubbles to the surface [47], whereas nonvolatile water-soluble PSCs are diluted and transported away from their sources [48]. High levels of soil moisture also affect the availability of oxygen for roots and soil microorganisms, eventually generating anaerobic conditions, which influence both plant PSC-producing and microbial PSC-decomposing metabolisms [45,49]. By contrast, drought may decrease the concentration of volatile PSCs in the soil due to the increase in the volume of air in the soil and better ventilation at the soil surface. For example, sesquiterpenes emitted by maize diffuse faster and farther at low moisture levels [50].

Climate change can significantly impact the movement and lifetime of PSCs in soils, either by affecting abiotic drivers directly or by affecting the macro- and microbiotic communities involved in the liberation, processing, and transport of PSCs [51] (also see section 'Plant–Soil Microorganism Interactions'). For example, increasing soil temperature will enhance PSC diffusion and exchange rates and alter state and partitioning equilibria between surfaces. Extreme weather events, such as thunderstorms and drought events, are expected to increase in both frequency and intensity, which will amplify the asymmetric transport and concentration build-up of polar and/or nonpolar PSCs in soils. Determining the presence and fate of PSCs in soil is an under-researched area but one that is highly relevant to evaluating their ecological and evolutionary impact on the belowground interactions discussed later. Understanding the main environmental factors driving these processes is necessary to assess how climate change will alter belowground interactions mediated

Box 1. Sampling of PSCs for Identification and Quantification

The heterogeneous chemical and physical nature of soil creates spatial differences that complicate representative sampling. In addition, PSCs have a high diversity of functional groups, volatilities, and polarities. Thus, their belowground presence can be in air, in pore water, or adsorbed to solid matter. Therefore, representative sampling may require a combination of sampling techniques. Such techniques for PSCs in soil include extraction (solvent or solid phase), head-space analysis, and purge-and-trap techniques [7].

Solvent extraction relies on the principle of 'like dissolves like'. Thus, polar compounds are extracted in polar solvents (e.g., water or methanol) and nonpolar compounds in nonpolar solvents (e.g., n-hexane or dichloromethane). However, several hundreds of grams of soil may be needed for the representative sampling of PSCs with low concentrations in soil [110]. Given that dilution beyond detection limits may occur, subsequent sample concentration by solid-phase extraction (SPE) or evaporation (with the risk of loss of volatiles) may be necessary. Emission of PSCs directly from roots has been investigated using primarily solid-phase microextraction (SPME) or adsorption tubes (with e.g., Tenax) coupled with gas chromatograph–mass spectrometry (GC-MS) analysis in several studies, as reviewed in [7].

SPME, head-space analysis, and purge-and-trap methods avoid the dilution effect of solvents but are more selective in the compounds sampled. SPME relies on the equilibrium between a fiber coated with a sorbing material and most often the gas phase (potentially also water or solid phase). This technique allows *in situ* sampling for evaluating small-scale spatial differences. The sorbing material determines the selectivity of the compounds sampled [111], whereas soil type, water content, and pH influence the equilibrium. Stir-bar sorptive extraction (SBSE), where a magnetic rod is coated with sorbing material, may provide up to 1000-fold higher sensitivity, but requires thermal desorption for subsequent instrument introduction. SBSE is useful for extraction from water, as demonstrated for many organic pollutants [112]. Identifying the mode of transport of PSCs (i.e., in gas or water phase) could be accomplished by sampling the soil gas phase using SPME and subsequently washing the soil and extracting using SBSE.

Collecting only head spaces using an air-tight syringe is a potential way to sample only volatile PSCs (i.e., VOCs). However, the concentration of VOCs from soil may be <10 μg m^{-3}, which is below the detection limit for head-space analysis. This limitation may be overcome with purge-and-trap methods recommended for analysis when concentrations are <200 μg kg^{-1} [113], which were recently applied for sampling isoprene, monoterpenes, and sesquiterpenes in forest soil [19].

by PSCs (Figure 1). Different methods may be needed for different types of PSC, depending on their solubility and volatility (Box 1 and Table 1).

Ecological and Evolutionary Impacts of PSCs on Belowground Species Interactions

Similar to the functions of PSCs aboveground, key organismal interactions in soil (i.e., plant–plant, plant–soil microorganism, and plant–soil invertebrate interactions) are also mediated by PSCs. The identity, concentration, and composition of PSCs belowground have pivotal roles in species interactions and community structuring, and ultimately affect entire ecosystem processes.

Plant–Plant Interactions

PSCs mediate both competitive and facilitative interactions among plants. **Allelopathic effects** of PSCs released by a focal plant to the local soil environment can inhibit the germination and growth of competitors, giving the focal plant a competitive advantage for space and nutrients [52]. The 'Novel Weapons' hypothesis [53] is based on the idea that invasive plants release **allelochemicals** that the native community has not previously encountered and that give the invader a competitive advantage. Allelopathic effects of PSC have helped some invasive plant species to create virtual monocultures in the habitats they invade. For example, production of **phytotoxic** phenolic acids, and di-, and sesqui-terpene lactones likely aided the invasive success of Canadian goldenrod *Solidago canadiensis* [54,55] and yellow star thistle *Centaurea solstitialis* [56]. Allelopathic effects are often less dramatic within the native ranges of plants because coexisting species have evolved either a tolerance of local PSCs or the ability to detoxify them [57].

PSCs released to the soil by one plant species may alter competitive hierarchies among neighboring plant species both directly when PSCs inhibit the growth of one species more than another, and indirectly by PSCs modifying the soil nutrient availability, which favors some species over others. For example, pine soil altered plant competition between spotted knapweed (*Centaurea stoebe)* and different grass species in favor of grasses. Soil containing pine litter had a higher content of phosphorus (P), which made the grasses more competitive against *Centaurea* [58]. Phenolic compounds and terpenes influence soil nitrogen (N) cycling because these compounds inhibit nitrification and the net N mineralization [59]. This could differentially favor plant species that differ in their preference for nitrate versus ammonium [60].

PSC-mediated plant–plant interactions also facilitate neighbor plants via so-called 'associational resistance' [61], where neighbor plants benefit from reduced attack by herbivores and pathogens due to the deterrent effects of the PSCs released by a focal plant. However, the PSCs in soil may also increase susceptibility to herbivores and pathogens if these plant enemies are attracted rather than repelled by the PSCs [52,61]. How these selective forces are balanced in the multispecies networks present in a natural field needs further study.

PSCs can vary among species, genotypes within species, and damaged and healthy tissue, and, thus, they contain information about the identity and state of the emitting plant [62]. Therefore, plants may use PSCs as a cue to recognize their neighbors and prepare for competitive encounters by adjusting their competitive growth towards or away from neighboring plants [63]. Root exudates and the chemicals they contain have been shown to mediate recognition of neighboring plants [64–66]. The competitive responses to such PSC-mediated neighbor recognition may depend on the history of coexistence between interacting plants [67], and for some plant species also on the genetic relatedness among interacting conspecifics [64,68]. However, we lack knowledge of the identity of which molecules in root exudates

mediate plant recognition and how plants perceive them. This knowledge is relevant to understand whether environmental changes in the soil may interfere with the ability of plants to detect their neighbors.

Spatial consistency of PSC production allows PSCs to act as selective agents on other species and favors the genotypes that respond most beneficially to the effects of frequently encountered PSCs. For example, the grass *Bromus erectus* is a frequent neighbor of *T. vulgaris*, which releases either phenolic or nonphenolic monoterpenes to the local soil environment. *Bromus* plants originating from sites where their thyme neighbors produce a nonphenolic monoterpene germinate and grow better in soil rich in nonphenolic thyme monoterpenes compared with similar soil rich in phenolic thyme monoterpenes [69]. Hence, plants can adapt to the chemical environment imposed by frequent neighbors, and this adaptation is compound specific. Changes in the consistency of frequently encountered PSCs could disrupt such adaptive responses.

From Pairwise Plant–Plant Interaction to Communities

The PSCs released to the soil from different plant genotypes and species create a mosaic of soil chemical environments. Given that different chemical environments favor different species due to the pairwise competitive and facilitative interactions described earlier, variation in chemical types both within and among populations can contribute to local and regional species richness. For example, the chemical diversity of Scots pine (*Pinus sylvestris*) needle terpenes was positively correlated with plant species richness in the vegetation under the trees, and trees with different needle chemistry associated with a different plant species composition [70,71]. Chemical diversity of *T. vulgaris* also correlated with plant species richness and composition of the vegetation around thyme plants. Plant species richness was higher, and species composition more similar around thyme plants compared with a thyme-free area only a few meters away. However, species richness and species composition differed in area with the different thyme chemical types [72]. These examples suggest that the chemical types of dominant plants have an 'extended phenotype' [73,74], where the chemicals released from a focal plant can shape the surrounding vegetation. However, we need more experimental manipulation studies investigating the consistency of the effects of variation in PSC released by foundation plants on the richness and composition of associated plant communities. These studies will allow us to better understand the cause and effect of variation in PSC and to predict the potential cascading effects of qualitative and quantitative changes in PSCs.

Plant–Soil Microorganism Interactions

A large proportion of the nutrients present in the soil are not immediately available for plants but require enzymes to degrade them into usable parts, and soil microorganisms are major suppliers of these enzymes [75]. In addition, soil symbionts, such as mycorrhizal fungi and rhizobacteria, are important regulators of plant productivity, especially in nutrient-poor ecosystems, where they are responsible for 5–75% of N and up to 80% of P acquired by plants annually [76].

The importance and complexity of the interactions between plants and soil microbes have been acknowledged for a long time, but only more recently has it been appreciated that many of these interactions are mediated by PSCs [77]. Given the importance of such interactions, it is likely that plants have evolved strategies to recognize friend from foe and to harness useful partners across distances. For example, flavonoids produced by legumes have a fundamental role in attracting rhizobia and promoting the production of Nod-factor molecules, which are critical for nodulation [78]. In this process, both plants and microbes produce chemical signals that allow the plant to recognize the rhizobia as a friend and prevent the activation of immune responses upon initiation of the symbiosis [79]. When rhizobia are not found in the proximity of the rhizosphere and

distances between the roots of individual plants and their symbionts are too large to be covered by root exudates, legumes can resort to the help of an intermediary to carry the symbionts to them [80]. The production of volatile PSCs by the legume *Medicago truncatula* attracts individuals of the free-living nematode *Caenorhabditis elegans*, which harbors the rhizobium *Sinorhizobium meliloti* either on its cuticle or in its intestine. Isoflavonoids produced by the plant prime the rhizobium to initiate the symbiosis when the nematode is near the roots [80].

Not only can plants affect the composition of specific soil microbial communities via PSC, but they can also alter it when exposed to stress, such as herbivore attacks [77]. In many plant species, the presence of pathogens or root-feeding fungi corresponds with a shift in the soil microbial composition close to the rhizosphere. This is a consequence of both the production of specific antimicrobial compounds by the plant rhizosphere and the recruitment of favorable bacteria. The blend of PSCs produced by the graminoid *Carex arenaria* shifts toward a higher concentration of terpenes and terpenoids to attract specific bacteria with antifungal properties when the roots are infected with the pathogenic fungus *Fusarium culmorum* [81]. Bacteria successfully rallied by the plant can gain from this interaction via the additional nutrients obtained by feeding on the plant pathogens [81]. Recent studies compared wild-types of *Arabidopsis thaliana* with mutants that are unable to synthesize PSCs involved in induced systemic resistance against soil pathogens. Metagenome analysis of root microbiome associated with wild-types versus mutants showed substantially different community composition, indicating the important role of PSC in modulating the composition of root microbiome [82].

PSC-induced shifts in the composition of soil microbiota can also be activated by attacks to plant leaves. For example, infestations of white flies (*Bemisia tabaci*) on pepper plants led to a change in belowground microflora, enhancing the antipathogen responses [83].

The interactions between plants and soil microorganisms are not unidirectional, because soil microbes can also emit chemical compounds that can be detected and used by plants. For example, secondary compound emissions from soil microflora may help the woodland strawberry, *Fragaria vesca*, to detect nutrient-rich patches before rooting. Stolons can preferentially develop toward substrates emitting unbranched fatty acids and avoid substrates with higher concentrations of terpenes and aldehydes [84].

Many PSCs are used by bacteria and fungi as a source of nutrients [85], and soil microorganisms can alter and repurpose the PSCs released by plants. In the legume *Lotus japonicus,* inoculation with its symbiont *Mesorhizobium loti* led to a change in the profile of the plant phenolic compounds [86]. The soil bacterial community associated with vetiver, *Chrysopogon zizanioides,* uses the sesquiterpenes produced by the grass as a source of carbon and, after metabolizing them, releases several compounds from vetiver oil [87]. Colonization of roots by arbuscular mycorrhizal fungi can increase the production of glucosinolates, phenolic acids, and flavonoids in several plant species [88,89].

On a larger scale, the ability of soil microbial communities to process and degrade plant secondary metabolites can have important consequences on plant communities and ecosystem stability. For example, soil microorganisms can either favor or hinder the proliferation of invasive plant species, depending on their ability to degrade the allelopathic compounds produced by invasive plants [90].

A high species-specificity of plant–microbe interactions suggest that single plants shape their soil bacterial communities, and microorganisms respond to subtle genetic variation in plants. In

cottonwood trees *Populus angustifolia*, 70% of the variation in soil microbial community composition was explained by plant genotype identity [91].

Although there is still much that we need to understand about the complex interactions between PSC and roots microbiome, progress is being made in elucidating the factors that drive the composition of root-inhabiting bacterial communities [92]. Future steps will need to go beyond pairwise interactions between plants and a specific guild of soil microorganism, targeting instead how whole communities of soil microorganisms are affected by PSC and, in turn, affect plant communities. Climate change may mediate shifts in plant–soil microorganism interactions via shifts in the chemical profile of plants and soil microorganisms. Such studies are valuable because the positive effect of certain plant–soil microorganism interactions can be harnessed to either enhance agricultural practices or as biocontrol agents. Understanding how to engineer beneficial soil communities for plant community conservation, sustainable agriculture, and the preservation of native communities require extensive experimentation and in-depth understanding of potential unintended consequences of such manipulations.

Plant–Soil Invertebrate Interactions

Many of the interactions between plants and soil invertebrates are mediated by PSCs, often with significant effects on soil processes that determine soil function and plant productivity. Two major ways can be distinguished through which PSCs mediate the interactions between plants and soil invertebrates. First, soil organisms can be exposed to substantial input of PSCs from aboveground plant tissues, through PSCs leaching from foliar tissue and PSC-rich litter deposition. These PSCs are mostly known as feeding repellents, and many of them have toxic effects on aboveground insect herbivores [93]; the available evidence indicates that they also have toxic effects on nontarget organisms, such as soil invertebrates [94,95]. Toxic effects can occur if PSCs diffuse across the cuticle or if animals ingest PSC-rich litter, with the main route of exposure determined by cuticle morphology and diet of the soil invertebrate and by the chemical properties of the PSC (see Table 1 for mode of toxicity). Nonpolar (lipophilic) volatile PSCs likely enter animal bodies primarily by simple diffusion across the cuticle and easily partition into cellular membranes [94]. High concentrations of nonpolar PSCs can occur regularly in soil, especially in older litter and near roots, as is the case for terpenoids (1–5 mg g^{-1} fresh weight) [2]. The likelihood of exposure is increased because terpenoids remain in the litter layer for several months until fully decomposed [96]. Exposure to polar PSCs is mainly through ingestion of litter or roots, for example in the case of isothiocyanates. Isothiocyanates have high toxicity towards nontarget soil invertebrates, including beneficial macrodetritivores that promote nutrient cycling and soil fertility [97]. Currently, the relative importance of the two exposure routes, either via contact with volatile or water-dissolved PSCs in pore water and diffusion across the cuticula, or via ingestion of PSC-rich litters by soil fauna, and how this affects soil fauna functional community composition is poorly known.

An unexplored aspect of lipophilic PSCs is that their spread can be facilitated by animal transport. Soil animals can accumulate high internal concentrations of these PSCs in the vicinity of roots and litter and subsequently deliver them to other soil microenvironments with lower chemical activity as they move away from the PSC source. Aquatic Protozoa have demonstrated such animal-facilitated transport [98], but more research is needed to explore this phenomenon mediated by soil animals. To explore the toxicity of PSCs to soil invertebrates under field conditions, more precise analytical determinations of concentrations of PSCs and their degradation products in the environment are needed. This necessitates new experimental systems of exposure, such as by using the framework of chemical activity for volatile compounds [94].

The second way in which PSCs can mediate plant invertebrate interactions in the soil is by targeted release of PSCs from the roots. These PSCs can attract or deter soil invertebrates and serve as chemical signals released by the plant to control trophic interactions with plant-parasitic nematodes, root herbivores, and their predators. The use of PSCs in tritrophic interactions between plants and belowground organisms may be similar to the extensively studied chemically mediated interactions between plants, foliar herbivores, and their natural aboveground predators. Attack by root herbivores has been shown to induce a change in the quality and quantity of PSCs released by plant roots, which can then function as a signal to attract soil-dwelling predators and reduce the pest population [9,99,100]. Entomopathogenic nematodes often function as indirect defenses for plants [101,102]. For example, larvae of the longhorn beetle *Tetraopsis tetraophthalmus* feed on the roots of the common milkweed *Asclepias syriaca*, which releases volatiles into the soil that attract entomopathogenic nematodes, preventing the loss of plant biomass to herbivory [103]. Maize roots increase sesquiterpene exudation when attacked by insects, thus attracting entomopathogenic nematodes that feed on root herbivores [104]. However, notwithstanding this potential protective role of PSCs via attraction of beneficial nematodes, these PSCs can also attract the root herbivores themselves. The net effect of the attraction of both advantageous as well as detrimental nematodes on plant fitness has to be evaluated. Most examples of tritrophic interactions belowground involve entomopathogenic nematodes, but one of the few papers that reports on other soil fauna in tritrophic interactions is a case in which tulip bulbs infested by the rust mite *Aceria tulipae* emit volatile signals to the predatory mite *Neoseiulus cucumeris* [105]. Given the importance of chemical cues in belowground signaling, the effect of PSCs on tritrophic interactions is expected to be omnipresent, but, currently, we do not know enough about the spatial dimensions of volatile and water-dissolved PSCs effects on plant–root herbivore or parasite–herbivore interactions [106]. Abiotic gradients in soils are rather short and steep compared with aboveground systems, but we are currently ignorant of the spatial dimensions of volatile and water-dissolved PSC effects on plant–root herbivore or parasite–predator interactions.

PSCs and Belowground Coevolutionary Interactions

The examples discussed earlier demonstrate the different vital roles of PSCs in belowground plant–plant, plant–soil microorganism, and plant–soil invertebrate interactions. Some of these interactions are examples of the evolutionary adaptation of species to frequently encountered PSCs. Except for interactions specific to the rhizosphere, no studies have yet clearly shown whether adaptations of organisms to specific PSCs reciprocally alter PSC composition and production in plants (i.e., whether PSC-mediated belowground interactions result in pairwise or diffuse coevolution). Understanding whether belowground interactions are a source of selection on the chemical variation of PSC-producing plants is not straightforward because of the unspecific nature of the interactions. Belowground interactions often comprise multiple interactions and, therefore, estimating the consequences for fitness in PSC-producing plants is difficult. Also, for PSCs entering the soil via leaf leachates, the main selective force determining which PSCs are produced and in what concentration may largely depend on aboveground biotic interactions and local climate. In addition, the multifunctionality of PSCs extends beyond biotic interactions, which is a further complication in the evaluation of fitness consequences in PSC-producing plants. For instance, maize produces benzoxazinoid compounds not only as a defense against generalist herbivores, but also as chelating agents to acquire iron as a micronutrient. The larvae of western corn rootworm *Diabrotica virgifera*, are not injured by benzoxazinoids, but this specialist herbivore instead takes advantage of the presence of complexes between iron and these PSCs not only to detect the plant, but also to forage on these complexes [107].

Climate-induced shifts in the release of PSCs into the soil (Figure 1) may alter the outcome of within- and between-species interactions in ways that we still cannot predict. Long-term studies and the development of ecometabolomics [108] for elucidating the responses of PSC changes in plant communities due to warming and altered precipitation from climate change are particularly warranted for a better understanding of, and ability to predict, these shifts in PSCs production, diffusion in soil, and effects on belowground interactions.

Concluding Remarks and Perspectives

Soil is a theater of facilitation, symbiosis, and warfare deployed by plants and the various organisms living in it, and PSCs have a major role mediating many of these interactions. Plants and soil organisms have adapted to withstand, detoxify, or use the cocktail of PSCs originally meant to harm some of them. Therefore, understanding PSC-mediated relationships at the community scale and identifying the compounds involved in these interactions is important for better insight into the functioning of these systems and their evolution, especially in changing environments. High-throughput technologies are increasingly becoming available and may help to identify and determine the concentrations, transport, and modes of action of PSCs in soils. We encourage the creation of open, community-wide, curated, labeled, broad-spectrum PSC data sets across plant species and soils, because this would greatly increase the transfer of knowledge between scientists studying plants, microbes, and invertebrates in this biological belowground theatre. This could be a platform similar to, for example, the TRY plant trait data base[i], or PSC data sets could be added and incorporated to such established well-functioning platforms. The warranted study of the quantitative and qualitative effects of climate change on PSCs and their interactions with the environment and organisms would also benefit from these PSC data sets. The alterations of the production of PSCs due to climate change are highly variable, depending on dose, timing, PSC, and species. These changes in the production of PSCs can lead to unforeseen consequences for soil structure and function and can disturb biological feedbacks on soil chemistry and biology, perhaps even on atmospheric chemistry and climate [109], with a direction and intensity that warrants in-depth investigation (see Outstanding Questions).

Outstanding Questions

To what extent does the PSC plume originally released into a soil compartment become chemically degraded during diffusion and mixed with secondarily formed and other ambient PSCs? Does this dilution and mixing with other PSCs impair the signal quality for the receiving soil organisms or have they adapted to and even benefited from signal noise (e.g., to improve their foraging efficiency)?

How will climate change affect PSC production in both above- and belowground organs and how will these effects in turn affect the belowground interactions of associated communities of microbes, plants, and soil invertebrates?

What is the relative importance of specific PSCs for both plant–soil invertebrate and plant–plant interactions and can we understand their prevalence from knowledge of their mode of action? If the effects of PSC on associated species is compound specific, quantitative and qualitative changes in the input of PSC to the soil can have cascading effects on the richness and composition of belowground soil communities that may ultimately alter soil functioning.

What is the importance of a common coevolutionary history between PSCs in soil and the organisms exposed to them for shaping the outcome of their interactions?

How important are belowground interactions in determining the composition and concentration of PSCs released by the producer? In particular, what is the impact of selection (if any) that belowground interactions can exert on PSC composition and production in leaves relative to aboveground interactions and climate?

Resources

[i]www.try-db.org

References

1. Moore, B.D. *et al.* (2014) Explaining intraspecific diversity in plant secondary metabolites in an ecological context. *New Phytol.* 201, 733–750
2. Alessio, G.A. *et al.* (2008) Implications of foliar terpene content and hydration on leaf flammability of *Quercus ilex* and *Pinus halepensis*. *Plant Biol.* 10, 123–128
3. Gershenzon, J. and Dudareva, N. (2007) The function of terpene natural products in the natural world. *Nat. Chem. Biol.* 3, 408–414
4. Baldwin, I.T. *et al.* (2006) Volatile signaling in plant-plant interactions:" talking trees" in the genomics era. *Science* 311, 812–815
5. Hare, J.D. (2011) Ecological role of volatiles produced by plants in response to damage by herbivorous insects. *Annu. Rev. Entomol.* 56, 161–180
6. Ninkovic, V. *et al.* (2016) Decoding neighbour volatiles in preparation for future competition and implications for tritrophic interactions. *Perspect. Plant Ecol. Evol. Syst.* 23, 11–17
7. Delory, B.M. *et al.* (2016) Root-emitted volatile organic compounds: can they mediate belowground plant-plant interactions? *Plant Soil* 402, 1–26
8. Sasse, J. *et al.* (2018) Feed your friends: do plant exudates shape the root microbiome? *Trends Plant Sci.* 23, 25–41
9. Rasmann, S. and Turlings, T.C. (2016) Root signals that mediate mutualistic interactions in the rhizosphere. *Curr. Opin. Plant Biol.* 32, 62–68
10. Massalha, H. *et al.* (2017) Small molecules below-ground: the role of specialized metabolites in the rhizosphere. *Plant J.* 90, 788–807
11. Maruri-López, I. *et al.* (2019) Intra and extracellular journey of the phytohormone salicylic acid. *Front. Plant Sci.* 10, 423
12. Park, J.H. *et al.* (2013) Active atmosphere-ecosystem exchange of the vast majority of detected volatile organic compounds. *Science* 341, 643–647
13. Nguyen, T.B. *et al.* (2015) Rapid deposition of oxidized biogenic compounds to a temperate forest. *Proc. Natl. Acad. Sci.* 112, E392–E401
14. Spielmann, F.M. *et al.* (2017) Isoprene and α-pinene deposition to grassland mesocosms. *Plant Soil* 410, 313–322
15. Potier, E. *et al.* (2017) Chemical reaction rates of ozone in water infusions of wheat, beech, oak and pine leaves of different ages. *Atmos. Environ.* 151, 176–187
16. Gray, C.M. *et al.* (2010) Emissions of volatile organic compounds during the decomposition of plant litter. *J. Geophys. Res. Biogeosci.* 115, G03015
17. Omirou, M. *et al.* (2013) Dissipation of pure and broccoli-released glucosinolates in soil under high and low moisture content. *Eur. J. Soil Biol.* 56, 49–55

18. Staudt, M. *et al.* (2019) Compartment specific chiral pinene emissions identified in a Maritime pine forest. *Sci. Total Environ.* 654, 1158–1166
19. Mäki, M. *et al.* (2019) Boreal forest soil is a significant and diverse source of volatile organic compounds. *Plant Soil* 1–22
20. Gimsing, A.L. and Kirkegaard, J.A. (2009) Glucosinolates and biofumigation: fate of glucosinolates and their hydrolysis products in soil. *Phytochem. Rev.* 8, 299–310
21. Gimsing, A.L. *et al.* (2005) Extraction and determination of glucosinolates from soil. *J. Agric. Food Chem.* 53, 9663–9667
22. Cantor, A. *et al.* (2011) Low allelochemical concentrations detected in garlic mustard-invaded forest soils inhibit fungal growth and AMF spore germination. *Biol. Invasions* 13, 3015–3025
23. Possell, M. and Loreto, F. (2013) The role of volatile organic compounds in plant resistance to abiotic stresses: responses and mechanisms. In *Biology, Controls and Models of Tree Volatile Organic Compound Emissions* (Niinemets, U. and Monson, R.K., eds), pp. 209–235, Springer, Netherlands
24. Sobuj, N. *et al.* (2018) Impacts of elevated temperature and CO_2 concentration on growth and phenolics in the sexually dimorphic *Populus tremula* (L.). *Environ. Exp. Bot.* 146, 34–44
25. Holopainen, J.K. *et al.* (2018) Climate change effects on secondary compounds of forest trees in the northern hemisphere. *Front. Plant Sci.* 9, 1445
26. Peñuelas, J. and Estiarte, M. (1998) Can elevated CO_2 affect secondary metabolism and ecosystem function? *Trends Ecol. Evol.* 13, 20–24
27. Haberstroh, S. *et al.* (2018) Terpenoid emissions of two Mediterranean woody species in response to drought stress. *Front. Plant Sci.* 9, 1071
28. Bonn, B. *et al.* (2019) Biogenic isoprenoid emissions under drought stress: different responses for isoprene and terpenes. *Biogeosciences* 16, 4627–4645
29. Iason, G.R. *et al.* (2012) *The Ecology of Plant Secondary Metabolites: From Genes to Global processes*, Cambridge University Press
30. Song, W. *et al.* (2014) Laboratory and field measurements of enantiomeric monoterpene emissions as a function of chemotype, light and temperature. *Biogeosciences* 11, 1435–1447
31. Staudt, M. *et al.* (2004) Isoprenoid emissions of *Quercus* spp. (*Q. suber* and *Q. ilex*) in mixed stands contrasting in interspecific genetic introgression. *New Phytol.* 163, 573–584
32. Thompson, J.D. (2005) *Plant Evolution in the Mediterranean*, Oxford University Press
33. Pratt, J.D. *et al.* (2014) Genetically based latitudinal variation in *Artemisia californica* secondary chemistry. *Oikos* 123, 953–963
34. Brachi, B. *et al.* (2015) Coselected genes determine adaptive variation in herbivore resistance throughout the native range of *Arabidopsis thaliana*. *Proc. Natl. Acad. Sci.* 112, 4032–4037
35. Chen, J. *et al.* (2015) Chemotypic and genetic diversity in *Epimedium sagittatum* from different geographical regions of China. *Phytochemistry* 116, 180–187
36. Fischer, D. *et al.* (2014) Plant genetic effects on soils under climate change. *Plant Soil* 379, 1–19
37. Poelman, E.H. and Kessler, A. (2016) Keystone herbivores and the evolution of plant defenses. *Trends Plant Sci.* 21, 477–485
38. Thompson, J. *et al.* (2013) Evolution of a genetic polymorphism with climate change in a Mediterranean landscape. *Proc. Natl. Acad. Sci.* 110, 2893–2897
39. Thompson, J.D. *et al.* (2007) Ongoing adaptation to Mediterranean climate extremes in a chemically polymorphic plant. *Ecol. Monogr.* 77, 421–439
40. Adamczyk, B. *et al.* (2018) Plant secondary metabolites—missing pieces in the soil organic matter puzzle of boreal forests. *Soil Syst.* 2, 2
41. Kanerva, S. *et al.* (2008) Phenolic compounds and terpenes in soil organic horizon layers under silver birch, Norway spruce and Scots pine. *Biol. Fertil. Soils* 44, 547–556
42. Uteau, D. *et al.* (2013) Root and time dependent soil structure formation and its influence on gas transport in the subsoil. *Soil Tillage Res.* 132, 69–76
43. Provoost, J. *et al.* (2011) Henry's equilibrium partitioning between ground water and soil air: Predictions versus observations. *J. Environ. Prot. (Irvine, Calif.)* 2, 873–881
44. Hamamoto, S. *et al.* (2012) Organic matter fraction dependent model for predicting the gas diffusion coefficient in variably saturated soils. *Vadose Zone J.* 11, 1539–1663
45. Insam, H. and Seewald, M.S. (2010) Volatile organic compounds (VOCs) in soils. *Biol. Fertil. Soils* 46, 199–213
46. Matsuoka, K. *et al.* (2017) Reactive uptake of gaseous sesquiterpenes on aqueous surfaces. *J. Phys. Chem. A* 121, 810–818
47. Bourtsoukidis, E. *et al.* (2018) Strong sesquiterpene emissions from Amazonian soils. *Nat. Commun.* 9, 2226
48. Clauson-Kaas, F. *et al.* (2016) Ptaquiloside from bracken in stream water at base flow and during storm events. *Water Res.* 106, 155–162
49. Seewald, M.S. *et al.* (2010) Substrate-induced volatile organic compound emissions from compost-amended soils. *Biol. Fertil. Soils* 46, 371–382
50. Hiltpold, I. and Turlings, T.C. (2008) Belowground chemical signaling in maize: when simplicity rhymes with efficiency. *J. Chem. Ecol.* 34, 628–635
51. Glassman, S.I. *et al.* (2018) Decomposition responses to climate depend on microbial community composition. *Proc. Natl. Acad. Sci.* 115, 11994–11999
52. Effah, E. *et al.* (2019) Potential roles of volatile organic compounds in plant competition. *Perspect. Plant Ecol. Evol. Syst.* 38, 58–63
53. Callaway, R.M. and Ridenour, W.M. (2004) Novel weapons: invasive success and the evolution of increased competitive ability. *Front. Ecol. Environ.* 2, 436–443
54. Yuan, Y. *et al.* (2013) Enhanced allelopathy and competitive ability of invasive plant *Solidago canadensis* in its introduced range. *J. Plant Ecol.* 6, 253–263
55. Abhilasha, D. *et al.* (2008) Do allelopathic compounds in invasive *Solidago canadensis* sl restrain the native European flora? *J. Ecol.* 96, 993–1001
56. Irimia, R.E. *et al.* (2019) Biogeographic differences in the allelopathy of leaf surface extracts of an invasive weed. *Biol. Invasions* 21, 3151–3168
57. Inderjit *et al.* (2011) The ecosystem and evolutionary contexts of allelopathy. *Trends Ecol. Evol.* 26, 655–662
58. Metlen, K.L. and Callaway, R.M. (2015) Native North American pine attenuates the competitive effects of a European invader on native grasses. *Biol. Invasions* 17, 1227–1237
59. Smolander, A. *et al.* (2012) Nitrogen transformations in boreal forest soils—does composition of plant secondary compounds give any explanations? *Plant Soil* 350, 1–26
60. Boudsocq, S. *et al.* (2012) Plant preference for ammonium versus nitrate: a neglected determinant of ecosystem functioning? *Am. Nat.* 180, 60–69
61. Barbosa, P. *et al.* (2009) Associational resistance and associational susceptibility: having right or wrong neighbors. *Annu. Rev. Ecol. Evol. Syst.* 40, 1–20
62. Ninkovic, V. *et al.* (2019) Who is my neighbor? Volatile cues in plant interactions. *Plant Signal. Behav.* 14, e1634993
63. Novoplansky, A. (2019) What plant roots know? *Semin. Cell Dev. Biol.* 92, 126–133
64. Semchenko, M. *et al.* (2014) Plant root exudates mediate neighbour recognition and trigger complex behavioural changes. *New Phytol.* 204, 631–637
65. van Dam, N.M. and Bouwmeester, H.J. (2016) Metabolomics in the rhizosphere: tapping into belowground chemical communication. *Trends Plant Sci.* 21, 256–265
66. Kong, C.-H. *et al.* (2018) Plant neighbor detection and allelochemical response are driven by root-secreted signaling chemicals. *Nat. Commun.* 9, 1–9
67. Semchenko, M. *et al.* (2019) Soil biota and chemical interactions promote co-existence in co-evolved grassland communities. *J. Ecol.* 107, 2611–2622
68. Biedrzycki, M.L. *et al.* (2010) Root exudates mediate kin recognition in plants. *Commun. Integr. Biol.* 3, 28–35
69. Ehlers, B.K. and Thompson, J. (2004) Do co-occurring plant species adapt to one another? The response of *Bromus*

erectus to the presence of different *Thymus vulgaris* chemotypes. *Oecologia* 141, 511–518
70. Iason, G.R. *et al.* (2005) Does chemical composition of individual Scots pine trees determine the biodiversity of their associated ground vegetation? *Ecol. Lett.* 8, 364–369
71. Pakeman, J.R. *et al.* (2006) The extended phenotype of Scots pine *Pinus sylvestris* structures the understorey assemblage. *Ecography* 29, 451–457
72. Ehlers, B.K. *et al.* (2014) An allelopathic plant facilitates species richness in the Mediterranean garrigue. *J. Ecol.* 102, 176–185
73. Dawkins, R. (1982) *The Extended Phenotype*, Oxford University Press, Oxford
74. Whitham, T.G. *et al.* (2003) Community and ecosystem genetics: a consequence of the extended phenotype. *Ecology* 84, 559–573
75. Reynolds, H.L. *et al.* (2003) Grassroots ecology: plant–microbe–soil interactions as drivers of plant community structure and dynamics. *Ecology* 84, 2281–2291
76. Van Der Heijden, M.G. *et al.* (2008) The unseen majority: soil microbes as drivers of plant diversity and productivity in terrestrial ecosystems. *Ecol. Lett.* 11, 296–310
77. Mhlongo, M.I. *et al.* (2018) The chemistry of plant–microbe interactions in the rhizosphere and the potential for metabolomics to reveal signaling related to defense priming and induced systemic resistance. *Front. Plant Sci.* 9, 1–17
78. Bais, H.P. *et al.* (2006) The role of root exudates in rhizosphere interactions with plants and other organisms. *Annu. Rev. Plant Biol.* 57, 233–266
79. Hacquard, S. *et al.* (2017) Interplay between innate immunity and the plant microbiota. *Annu. Rev. Phytopathol.* 55, 565–589
80. Horiuchi, J.-I. *et al.* (2005) Soil nematodes mediate positive interactions between legume plants and rhizobium bacteria. *Planta* 222, 848–857
81. Schulz-Bohm, K. *et al.* (2018) Calling from distance: attraction of soil bacteria by plant root volatiles. *ISME J.* 12, 1252–1262
82. Stringlis, I.A. *et al.* (2018) MYB72-dependent coumarin exudation shapes root microbiome assembly to promote plant health. *Proc. Natl. Acad. Sci.* 115, E5213–E5222
83. Yang, J.W. *et al.* (2011) Whitefly infestation of pepper plants elicits defence responses against bacterial pathogens in leaves and roots and changes the below-ground microflora. *J. Ecol.* 99, 46–56
84. Waters, E.M. and Watson, M.A. (2015) Live substrate positively affects root growth and stolon direction in the woodland strawberry, *Fragaria vesca*. *Front. Plant Sci.* 6, 814
85. Junker, R.R. and Tholl, D. (2013) Volatile organic compound mediated interactions at the plant-microbe interface. *J. Chem. Ecol.* 39, 810–825
86. Rispail, N. *et al.* (2010) Secondary metabolite profiling of the model legume *Lotus japonicus* during its symbiotic interaction with *Mesorhizobium loti*. *Symbiosis* 50, 119–128
87. Del Giudice, L. *et al.* (2008) The microbial community of vetiver root and its involvement into essential oil biogenesis. *Environ. Microbiol.* 10, 2824–2841
88. Cosme, M. *et al.* (2014) Arbuscular mycorrhizal fungi affect glucosinolate and mineral element composition in leaves of *Moringa oleifera*. *Mycorrhiza* 24, 565–570
89. Pistelli, L. *et al.* (2017) Arbuscular mycorrhizal fungi alter the content and composition of secondary metabolites in *Bituminaria bituminosa* L. *Plant Biol.* 19, 926–933
90. Li, Y.-P. *et al.* (2015) Soil microbes alleviate allelopathy of invasive plants. *Sci. Bull.* 60, 1083–1091
91. Schweitzer, J.A. *et al.* (2008) Plant–soil–microorganism interactions: heritable relationship between plant genotype and associated soil microorganisms. *Ecology* 89, 773–781
92. Walters, W.A. *et al.* (2018) Large-scale replicated field study of maize rhizosphere identifies heritable microbes. *Proc. Natl. Acad. Sci.* 115, 7368–7373
93. Mithöfer, A. and Boland, W. (2012) Plant defense against herbivores: chemical aspects. *Annu. Rev. Plant Biol.* 63, 431–450
94. Trac, L. *et al.* (2019) Headspace passive dosing of volatile hydrophobic organic chemicals from a lipid donor – linking their toxicity to well-defined exposure for an improved risk assessment. *Environ. Sci. Technol.* 53, 13468–13476
95. van Ommen Kloeke, A.E. *et al.* (2012) Time-related survival effects of two gluconasturtiin hydrolysis products on the terrestrial isopod *Porcellio scaber*. *Chemosphere* 89, 1084–1090
96. Kainulainen, P. and Holopainen, J. (2002) Concentrations of secondary compounds in Scots pine needles at different stages of decomposition. *Soil Biol. Biochem.* 34, 37–42
97. Jensen, J. *et al.* (2010) The toxic effects of benzyl glucosinolate and its hydrolysis product, the biofumigant benzyl isothiocyanate, to *Folsomia fimetaria*. *Environ. Toxicol. Chem.* 29, 359–364
98. Gilbert, D. *et al.* (2014) Co-transport of polycyclic aromatic hydrocarbons by motile microorganisms leads to enhanced mass transfer under diffusive conditions. *Environ. Sci. Technol.* 48, 4368–4375
99. Wenke, K. *et al.* (2010) Belowground volatiles facilitate interactions between plant roots and soil organisms. *Planta* 231, 499–506
100. Kergunteuil, A. *et al.* (2019) Environmental gradients and the evolution of tri-trophic interactions. *Ecol. Lett.* 22, 292–301
101. Laznik, Ž. and Trdan, S. (2016) Attraction behaviors of entomopathogenic nematodes (*Steinernematidae* and *Heterorhabditidae*) to synthetic volatiles emitted by insect damaged potato tubers. *J. Chem. Ecol.* 314-322
102. Tonelli, M. *et al.* (2016) Attraction of entomopathogenic nematodes to sugarcane root volatiles under herbivory by a sap-sucking insect. *Chemoecology* 59–66
103. Rasmann, S. *et al.* (2011) Direct and indirect root defences of milkweed (*Asclepias syriaca*): trophic cascades, trade-offs and novel methods for studying subterranean herbivory. *J. Ecol.* 99, 16–25
104. Rasmann, S. *et al.* (2005) Recruitment of entomopathogenic nematodes by insect-damaged maize roots. *Nature* 434, 732
105. Aratchige, N. *et al.* (2004) Below-ground plant parts emit herbivore-induced volatiles: olfactory responses of a predatory mite to tulip bulbs infested by rust mites. *Exp. Appl. Acarol.* 33, 21–30
106. Erb, M. *et al.* (2013) The role of plant primary and secondary metabolites in root-herbivore behaviour, nutrition and physiology. In *Advances in Insect Physiology*, pp. 53–95, Elsevier
107. Hu, L. *et al.* (2018) Plant iron acquisition strategy exploited by an insect herbivore. *Science* 361, 694–697
108. Penuelas, J. and Sardans, J. (2009) Ecological metabolomics. *Chem. Ecol.* 25, 305–309
109. Heald, C. *et al.* (2008) Predicted change in global secondary organic aerosol concentrations in response to future climate, emissions, and land use change. *J. Geophys. Res.-Atmos.* 113, D05211
110. Christensen, P. *et al.* (2018) Chemical fingerprinting of mobile volatile organic compounds in soil by dynamic headspace - Thermal Desorption - Gas Chromatography - Mass Spectrometry. *LCGC Europe* 31, 190–201
111. Spietelun, A. *et al.* (2010) Current trends in solid-phase microextraction (SPME) fibre coatings. *Chem. Soc. Rev.* 39, 4524–4537
112. Ferreira, A.M.C. *et al.* (2011) Stir bar sorptive extraction of parabens, triclosan and methyl triclosan from soil, sediment and sludge with in situ derivatization and determination by gas chromatography–mass spectrometry. *J. Chromatogr. A* 1218, 3837–3844
113. EPA (1996) *Closed system purge-and-trap extraction for volatile organics in soil and waste samples*, US Environmental Protection Agency, pp. 1–24
114. Wezel, A.P.V. and Opperhuizen, A. (1995) Narcosis due to environmental pollutants in aquatic organisms: residue-based toxicity, mechanisms, and membrane burdens. *Crit. Rev. Toxicol.* 25, 255–279
115. Glasius, M. and Goldstein, A.H. (2016) Recent discoveries and future challenges in atmospheric organic chemistry. *Environ. Sci. Technol.* 50, 2754–2764
116. Barreira, L.M.F. *et al.* (2015) Field measurements of biogenic volatile organic compounds in the atmosphere by dynamic solid-phase microextraction and portable gas chromatography-mass spectrometry. *Atmos. Environ.* 115, 214–222

117. Bäck, J. *et al.* (2010) Variable emissions of microbial volatile organic compounds (MVOCs) from root-associated fungi isolated from Scots pine. *Atmos. Environ.* 44, 3651–3659
118. de Rijke, E. *et al.* (2006) Analytical separation and detection methods for flavonoids. *J. Chromatogr. A* 1112, 31–63
119. Weston, L.A. and Mathesius, U. (2013) Flavonoids: their structure, biosynthesis and role in the rhizosphere, including allelopathy. *J. Chem. Ecol.* 39, 283–297
120. Heath, M.C. (2000) Hypersensitive response-related death. *Plant Mol. Biol.* 44, 321–334
121. Cesco, S. *et al.* (2010) Release of plant-borne flavonoids into the rhizosphere and their role in plant nutrition. *Plant Soil* 329, 1–25
122. Carlsen, S.C. *et al.* (2012) Fate in soil of flavonoids released from white clover (*Trifolium repens* L.). *Appl. Environ. Soil Sci.* 2012, 1–10
123. Halkier, B.A. and Gershenzon, J. (2006) Biology and biochemistry of glucosinolates. *Annu. Rev. Plant Biol.* 57, 303–333
124. Aniszewski, T. (2015) *Alkaloids: Chemistry, Biology, Ecology, and Applications*, Elsevier
125. Klein-Junior, L.C. *et al.* (2016) Enlarging the bottleneck in the analysis of alkaloids: a review on sample preparation in herbal matrices. *TrAC Trends Anal. Chem.* 80, 66–82